

“Direct Measurement of CO₂ Fluxes in Marine Whittings”

Final Report

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Abstract

Clean, affordable energy is a requisite for the United States in the 21st Century. Scientists continue to debate over whether increases in CO₂ emissions to the atmosphere from anthropogenic sources, including electricity generation, transportation and building systems may be altering the Earth's climate. While global climate change continues to be debated, it is likely that significant cuts in net CO₂ emissions will be mandated over the next 50-100 years. To this end, a number of viable means of CO₂ sequestration need to be identified and implemented. One potential mechanism for CO₂ sequestration is the use of naturally-occurring biological processes. Biosequestration of CO₂ remains one of the most poorly understood processes, yet environmentally safe means for trapping and storing CO₂. Our investigation focused on the biogeochemical cycling of carbon in microbial precipitations of CaCO₃. Specifically, we investigated modern whittings (microbially-induced precipitates of the stable mineral calcium carbonate) as a potential, natural mechanism for CO₂ abatement. This process is driven by photosynthetic metabolism of cyanobacteria and microalgae. We analyzed net air: sea CO₂ fluxes, net calcification and photosynthetic rates in whittings. Both field and laboratory investigations have demonstrated that atmospheric CO₂ decreases during the process of microbial calcification.

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INTRODUCTION

President Bush recently announced the National Climate Change Technology Initiative (NCCTI). The objective of the initiative is to develop and apply technologies to reduce the build up of greenhouse gases in the atmosphere, with the ultimate goal of stabilizing the concentration of greenhouse gases in the atmosphere. Clearly many technologies will have to be explored and ultimately implemented in the abatement and stabilization of greenhouse gases. Our research addresses one method to sequester carbon in aqueous environments, including both marine and freshwater systems.

The bulk of carbon on earth is stored in rocks and sediment, while only a small fraction is within the mobile reservoirs of atmosphere, oceans, and the terrestrial biosphere. The fraction of carbon present as CO₂ in the atmosphere is critical for photosynthesis and this provides a natural mechanism for CO₂ fixation. The study of sinks of CO₂ has been a major concern in recent years owing to the inevitability of global change in climate and society's concern over the “greenhouse effect.” Human induced global change has reached rates similar to those of “geologic catastrophes” in the past. Clearly data are needed to assess a variety of sinks of CO₂. Investigating natural mechanisms of CO₂ fixation may provide a means for partial abatement of anthropogenic CO₂.

Background

Researchers at the University of South Florida, Molecular Paleontology and Biomineralization Laboratory and more recently at the U.S. Geological Survey have been investigating Bahamian Whitings, large scale floating patches of lime mud (CaCO₃). Based on data collected from our numerous research cruises, we have observed that whitings are associated with blooms of cyanobacteria and unicellular green algae (such as *Synechococcus*, *Synechocystis*, and *Chlorella*), and that these organisms are capable of inducing carbonate mineral precipitation in the water column (Robbins and Blackwelder, 1992; Robbins and Yates, unpublished data). These species have also been implicated in the formation of freshwater whitings (Thompson and Ferris, 1990; Thompson et al., 1990). Laboratory experiments by Yates and Robbins (1998) reveal that a single bloom of calcifying picoplankton can, potentially, generate several thousand kilograms of CaCO₃ sediment per day. Microbial calcification has also been implicated in the production of numerous, thick sequences of modern and ancient lime-mud deposits (Cloud 1961, Meeder 1979, Horodyski and Mankiewicz 1990, Knoll and Swett 1990, Kazmierczak et al. 1994, and Davis et al. 1995). Despite the potential impact that microbial calcification has had on carbonate sediment budgets and inorganic carbon cycling, little had been known on the effects of this process on carbon cycling.

Traditionally, the precipitation of calcium carbonate has been expressed as the inorganic chemical reaction $\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ indicating that CO₂ is evolved during precipitation. It has, thus, been generally accepted that inorganic calcium carbonate

precipitation represents a source of CO₂ on short geological time scales and a sink for inorganic carbon on geologically long time scales (10⁶ to 10⁹ years) since HCO₃⁻ is derived from hydration of CO₂ or dissolution of calcium carbonate via the reverse reaction (Sarmiento and Bender 1994). Berger (1982) first introduced the Coral Reef Hypothesis as an explanation for the increase of carbon dioxide in the atmosphere during deglaciation. He suggested that as coral reefs are re-established on flooded continental shelves, CO₂ is generated via precipitation of biogenic calcium carbonate via $\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$. This mechanism for evolution of CO₂ via biogenic CaCO₃ precipitation has been used as a generalization for calcification by nearly all species of calcium carbonate producing organisms.

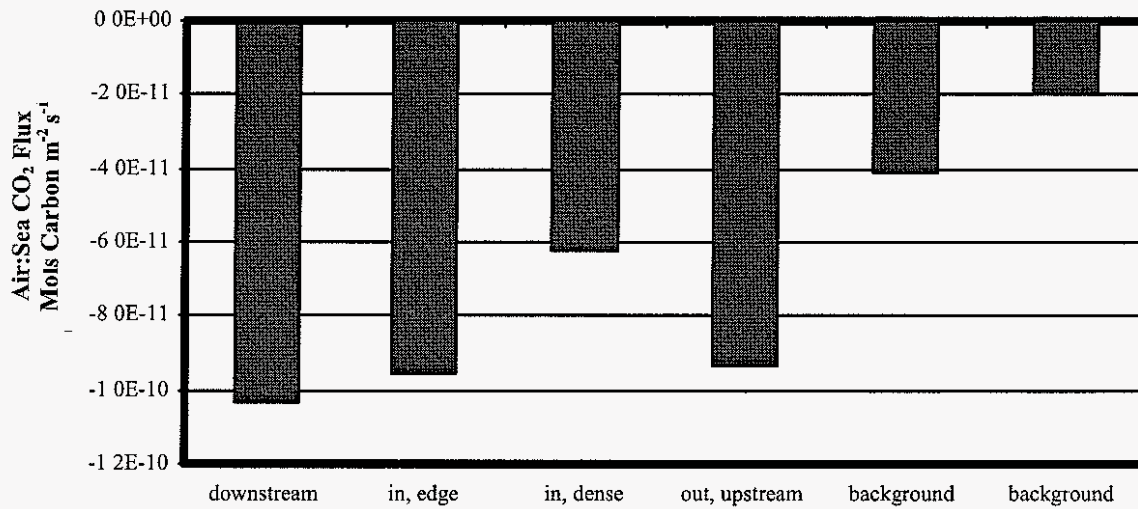
Goal of Study

As a major objective of our study, we addressed the question, are naturally occurring microbial precipitations sinks or sources of CO₂? We used measurements of aqueous and atmospheric pCO₂, alkalinity, pH, dissolved oxygen, salinity and cell counts to calculate calcification, dissolution, photosynthesis and respiration, and air:sea CO₂ fluxes associated with Bahamian whittings events and adjacent clear water.

RESULTS

During our year of Department of Energy funding we utilized a floating bell environmental isolation chamber to measure air:sea carbon dioxide fluxes and also focused on implementing newly developed equipment (SHARQ) designed to enable systematic geochemical analyses of in situ microbial precipitation events such as whittings. Measurements at this level of resolution have been non-existent in the past due to technological limitations. For the first time, 24-hour measurements of carbonate sediment production, photosynthesis and respiration in whittings were achieved. Our initial results indicate that microbial blooms are capable of producing large quantities of sediment during a single day. Additionally, we have made the first, direct air:sea pCO₂ gas flux measurements associated with whiting events. Gas flux measurements were made along transects through whittings including water outside of the whiting boundaries. These results indicate that microbial precipitation associated with the whiting process draws down CO₂, at an average rate of 8.1×10^{-11} moles CO₂ m⁻² sec⁻¹ (Figure 1).

CO₂ Gas Fluxes in Whittings and Adjacent Clear Water 9/2/99



CO₂ Gas Fluxes in Whittings and Adjacent Clear Water 6/13/99

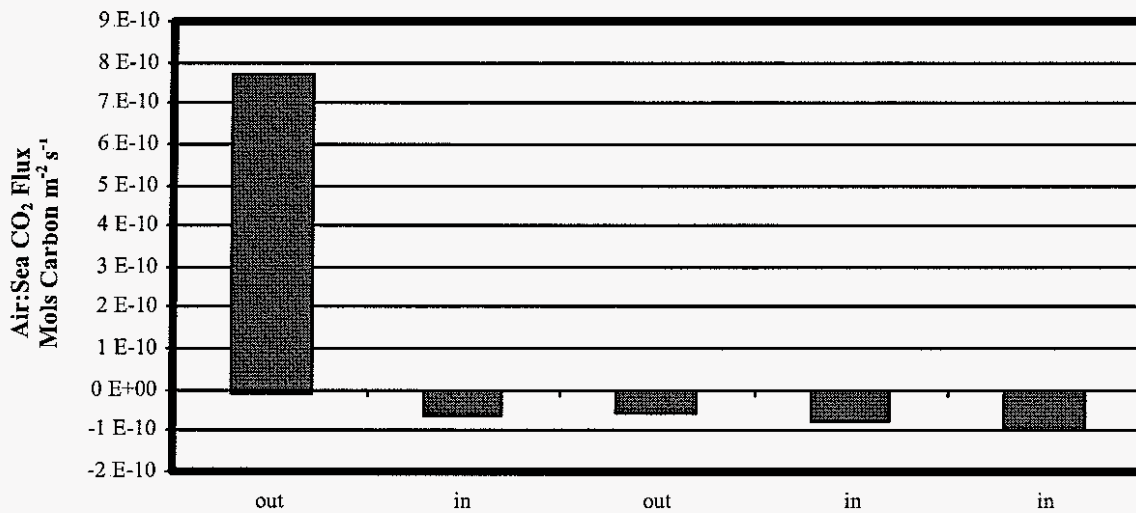


Figure 1. Direct measurements of air:sea CO₂ gas fluxes in whittings on the Bahama Bank in June and September indicate uptake of atmospheric CO₂ in whittings. Positive numbers indicate flux of CO₂ from water to air. Negative numbers indicate flux of CO₂ from air to water. Background measurements were taken in the same location on days when whittings were not present.

Based on average aerial coverage of whittings for each month of the year (Tao, 1994), we calculate an average uptake of carbon as CO_2 in whittings of approximately 1.6 tons carbon yr^{-1} (Table 1). Using on field measurements of calcification rates in whittings and aerial coverage data (Tao, 1994), we calculated average sequestration of carbon as calcium carbonate of approximately 5682 tons carbon yr^{-1} (Table 2). In natural systems such as whittings, the inorganic carbon source for calcification is derived from both atmospheric CO_2 and an unlimited supply of dissolved inorganic carbon (bicarbonate and carbonate) in seawater. Therefore, carbon uptake potential in a natural setting is represented by both CO_2 uptake (Table 1) and carbon precipitated as calcium carbonate (Table 2). Establishing this process in an industrial setting will isolate the microorganism from an unlimited supply of seawater inorganic carbon. The source of inorganic carbon for microbial mineral production, cell growth and reproduction will be derived only from input of industrial carbon waste (CO_2 , HCO_3^- , CO_2). Carbon can then be sequestered and stored as a benign, environmentally compatible CaCO_3 mineral product that can be easily disposed of or recycled.

Results from our field data acquired indicate that photosynthetically driven microbial calcification sequesters CO_2 . This is the first time a biogenic calcification mechanism has been identified that does not comply with generally accepted theories of CO_2 production during calcification.

USE OF SHARQ:

Using the Submersible Habitat for Analyzing Reef Quality (SHARQ)(patent pending), a clear, polyvinyl tent was used to trap whiting water from the underlying benthic substrate (Figure 2). The SHARQ has an internal circulation system and a flow-through analytical

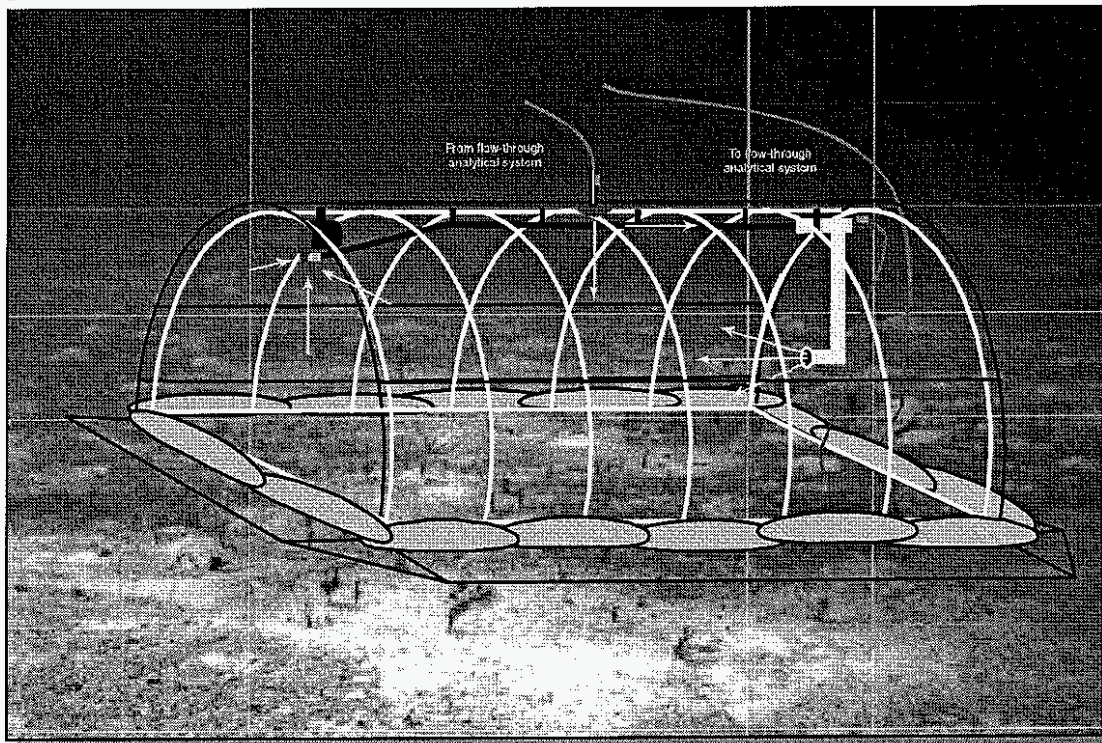


Figure 2. Schematic drawing of SHARQ (Submersible Habitat for Analyzing Reef Quality) which was used to sample whittings water in situ.

system to prevent stagnation of water in the chamber and enable continuous monitoring of water chemistry at high sampling frequency and resolution. This enables in situ measurements of physical and chemical parameters required for calculating productivity and carbon cycling in whittings over 24-hour light/dark cycles.

Carbonate sedimentation and organic productivity (calcification, photosynthesis, and respiration) are most effectively determined from precise, in situ measurements of alkalinity, pH, temperature, conductivity, and air:sea CO₂ and O₂ gas fluxes using the techniques of Smith and Key (1975), Millero (1979), Barnes (1983), Gattuso et al. (1993), and Millero et al. (1993). Complete isolation of a portion of the water column within a whittings event allows in situ manipulation of environmental parameters (e.g. nutrients, salinity, pCO₂) for experimental investigations by performing simple chemical injections through the flow-through analytical system.

We have identified several species of cyanobacteria and unicellular green algae capable of calcification. In the future, calcification efficiency of individual microbial species could be examined using a floating microcosm designed to trap microbes and sediment particles while allowing them to interact with ambient water. This technique will allow us to monitor population dynamics, sediment production, and changes in water chemistry including pH, pCO₂, and air:sea CO₂ gas exchange over 24-hour light dark cycles. These data are critical for selection of microbial species that show the greatest potential for efficiency at sequestering carbon through biogenic calcification.

Yates (1996) provides a detailed discussion on potential physiological mechanisms for microbial calcification that result in sequestration of CO₂ during calcification. These mechanisms indicate that the efficiency of microbial calcification at sequestering CO₂ depends upon the degree of cellular influence on this process. For example, if the source of carbon for extracellular calcification comes from within cells rather than from the external media, then the rate at which calcification proceeds depends upon the rate at which carbon can be supplied to the precipitation reaction site from the cells. Additionally, the efficiency of microbial calcification at sequestering CO₂ directly will depend upon the microbes' ability to maintain high pH at the site of calcification and to recycle any carbon that may be produced during precipitation back into the calcification reaction. Carbon isotope experiments will be performed to determine the source of carbon for mineral production and quantify amounts provided from within cells versus the external media. It is well known that microorganisms preferentially utilize lighter carbon-12 isotopes and discriminate against heavier carbon-13 isotopes during photosynthetic uptake of carbon. This results in the relative enrichment of intracellular carbon with lighter carbon-12 and enrichment of ambient media with carbon-13. The fractionation effect may be used to quantify the amount of intracellular carbon incorporated into calcium carbonate. Microorganisms will be induced to calcify in media of known carbon isotopic composition. Incorporation of intracellular carbon into extracellular calcium carbonate should result in lower ratios of ¹³C/¹²C than in ambient media. The carbon isotopic composition of the media, microorganisms, and resulting precipitates will be analyzed via mass spectrometry and these ratios will be used to quantify the contribution of intracellular carbon to mineralization.

TECHNICAL APPROACH AND UNDERSTANDING

From the results of our research we have established that the potential exists for using microbial calcification technology for sequestering industrial carbon waste. Further development of this technology for commercialization requires the ability to induce and control this process in a laboratory setting and to identify mechanisms for optimizing its efficiency at

sequestering carbon. Further research in these directions will have to focus on field and laboratory investigations to:

- 1) Determine what controls induction of mineralization in a natural setting
- 2) Initiate and control the mineralization process in a laboratory setting
- 3) Quantify the effects of microbial calcification on media pH and carbon sequestration potential

SEQUESTRATION POTENTIAL OF WHITINGS

Direct measurements of air:sea CO₂ gas fluxes in whittings were made in June and September of 1999. Three to six measurements were made in each of three whittings studied. Average CO₂ flux measurements calculated for each whittings event were 3.3×10^{-6} g carbon m⁻² s⁻¹ (n = 6), 3.4×10^{-6} g carbon m⁻² s⁻¹ (n = 3), and 3.8×10^{-6} g carbon m⁻² s⁻¹ (n = 3), resulting in an overall average of 3.5×10^{-6} g carbon m⁻² s⁻¹ (n = 12). Tao (1994) calculated average daily areal coverage of whittings for each month of the year based on space shuttle photos of 885 whittings events on the Bahama Banks. Daily average coverage ranges from 16 – 76 km² day⁻¹. This information was used to estimate potential uptake of CO₂ in naturally occurring whittings on the Bahama Banks per month and per year based on minimum, maximum, and average CO₂ gas flux measurements reported above (Table 1.) Average uptake of carbon as CO₂ in whittings per year is approximately 1.6 tons carbon in a whiting area of approximately 17000 km². Average rates of calcification for 24-hour day/light cycles measured in July and September of 1999 were 6.2×10^{-2} g CaCO₃ m⁻³ hr⁻¹ and 7.5×10^{-3} g CaCO₃ m⁻³ hr⁻¹, respectively. Calculated rates of carbon precipitation as CaCO₃ based on these rates are 7.4×10^{-3} g carbon m⁻³ hr⁻¹ and 9.0×10^{-4} g carbon m⁻³ hr⁻¹ for June and September, respectively, (average = 4.2×10^{-3} g carbon m⁻³ hr⁻¹, n = 2). These rates of carbon precipitation were used to estimate potential sequestration of inorganic carbon as calcium carbonate in naturally occurring whittings per month and per year using data from Tao (1994) on areal distribution of whittings as described above (Table 2). Average sequestration of carbon as CaCO₃ is approximately 5682 tons carbon yr⁻¹.

	Whittings Area Km ² /day	CO ₂ uptake in whittings (tons C/month)		
		Average	Minimum	Maximum
January	30	0.086	0.081	0.093
February	30	0.081	0.076	0.087
March	58	0.166	0.157	0.181
April	75	0.215	0.203	0.234
May	76	0.218	0.206	0.237
June	32	0.089	0.084	0.097
July	33	0.095	0.089	0.103
August	31	0.089	0.084	0.097
September	16	0.044	0.042	0.048
October	72	0.207	0.195	0.224
November	50	0.139	0.131	0.151
December	52	0.149	0.141	0.162
Total	16988 km ² /year	1.578	1.49	1.71

Table 1. Estimated uptake of CO₂ in whittings based on a minimum CO₂ gas flux rate of 3.3×10^{-6} , maximum of 3.8×10^{-6} , and average of 3.5×10^{-6} g carbon m⁻² hr⁻¹.

	Whittings Area km ² /day @ 3m depth	Tons of C/month precipitated as CaCO ₃		
		Average	Minimum	Maximum
January	30	310	66	546
February	30	290	62	511
March	58	599	128	1056
April	75	775	166	1365
May	76	785	168	1384
June	32	320	69	564
July	33	341	73	601
August	31	320	69	564
September	16	160	34	282
October	72	744	159	1311
November	50	500	107	881
December	52	537	115	947
Total (tons/ year)		5682	1218	10012

Table 2. Estimated sequestration of carbon as CaCO₃ in whittings based on a minimum calcification rate of 9.0×10^{-4} , maximum of 7.4×10^{-3} , and average of 4.2×10^{-3} g carbon m⁻³ hr⁻¹.

Microbial calcification has the potential for providing a less costly means to addressing greenhouse gas emissions. As a natural process that can utilize industrial carbon waste [in the form of CO₂, HCO₃⁻, and CO₃²⁻], costly manipulation of waste products for incorporation into microbial precipitation reactions may be minimal. The resulting end product of microbial calcification, CaCO₃, is a benign mineral that can be easily discarded or utilized in a variety of economically viable products such as cements, ceramics, etc.

Carbon sequestration technology developed from microbial calcification will be based on biologically driven aqueous geochemical processes. The carbon sources for this process in natural settings are derived from equilibration of atmospheric CO₂ with seawater and HCO₃⁻ and CO₃²⁻ ions derived from weathering and dissolution of terrestrial carbonates that are carried to water bodies via surface runoff. Carbon sources required for microbial calcification must ultimately be in the form of dissolved inorganic carbon (HCO₃⁻, CO₃²⁻, H₂CO₃/dissolved CO₂). Carbon emissions (in the form of CO₂) from a variety of sources can easily be introduced to an aqueous system of calcifying microbes as either a gas or a liquid equilibrated with CO₂. Absorption rates of CO₂ into aqueous media can easily be controlled by manipulating pH and temperature. Elevation of pH increases the rate and amount of CO₂ absorbed. Microbial photosynthesis naturally elevates media pH facilitating absorption of CO₂. Field measurements of microbial calcification show no significant decrease in pH during calcification (Robbins and Yates, unpublished). However, laboratory measurements will be required to confirm and quantify the effects of microbial calcification on media pH.

Through field measurements and preliminary laboratory experiments we have gained insight into how the natural process of microbial calcification affects inorganic carbon cycling and atmospheric CO₂. Developing this process as a mechanism for impacting large quantities of greenhouse gases requires the ability to control this process and examine mechanisms for optimizing its efficiency at sequestering carbon. Future studies should include continued field and lab investigations that would focus on determining what controls induction of microbial calcification in nature, initiating and controlling this process in a lab setting, and further quantifying the effects of microbial calcification on media pH and carbon sequestration potential. This information is critical for examining the potential for optimizing the process as

a mechanism for carbon sequestration. As a biological process, a number of possibilities for process optimization exist including: selection of efficient microbial species, genetic or chemical manipulation of microbes to enhance metabolic processes affecting calcification reactions, nutrient availability and source, etc. These possibilities should be examined pending positive results in our efforts to control and manipulate microbial calcification in a lab environment.

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